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Over de additiviteit der atoomwarmte in binaire metaalverbindingen

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SUMMARY.

In these investigations, the validity was tested of the so-called additive law of NEUMANN-REGNAULT-KOPP, concerning the additivity of the specific heat in intermetallic compounds. SCHIMPF and later on SCHÜBEL had already proved this law for a long series of intermetallic compounds, below 0° C. as well as above this temperature. They conclude that the additive law is not really valid, but that it applies approximately. Many of the deviations observed remain within the limits of the experimental errors. A dependence of these deviations on the temperature could not be generally established.

TAMMANN and ROHMANN then tried to ascertain a connection between the deviations observed and other properties of the compounds, such as the contraction and the crystal structures as compared with those of the free components. All these attempts, however, led to no general results.

Several authors have already shown the deficiency of the supposed law in the case of solid-solutions and simple alloys, although it is not impossible, that some of the greater deviations might be caused by the presence of real compounds in such mixtures. For it will be seen from the results discussed in this thesis, as also from BOTTEMA's previously published data, that the values of the specific heats in the case of true „compounds” are not even approximately in accordance with the additive law.

BOTTEMA studied the compounds: $PtSn$, $AuSn$ and $AuSb_2$. In two cases: those of $PtSn$ and $AuSn$, he found that the molecular heats were smaller than the values calculated from the additive rule. The deviations amounted to 5—8 % and 2—5 % respectively. The compound $AuSb_2$ showed deviations in the opposite direction. Even within a small range of temperatures to a clearer dependence of the deviations on the temperature was stated. In the case of the mixed-crystals of Au and Ag , it may be remarked that the deviations at the

lower temperatures were very small and only more rapidly increasing above 600° C.

As still the exact values of the specific heats of the elements, of which some compounds are here examined, proved to be rather uncertain, it was necessary to redetermine the values mentioned. The questions as to the occurrence of true allotropic changes in zinc, could up till now not yet been completely settled. In the exact determination of specific heats of this metal in the interval of 100—360° C. (at the higher temperatures in vacuo) the presence of a discontinuity at about 170° C. could be confirmed. An irregularity, originally observed at 340° C., proved to disappear after thermal stabilisation of the metal at 360° C. The X-rays-analysis made by SIMON and VOHSEN, however, does not indicate that true allotropic changes here really occur. Perhaps the discontinuity observed is connected with some recrystallization-phenomena.

The measurements of the specific heats of magnesium at lower temperatures were made with an unprotected lump of the metal, and from 350° C. upwards with a piece of the metal enclosed in a platinum-vacuum-crucible. The values, obtained with the unprotected lump at temperatures from 350° C. upwards are all about 0,3—0,7 % higher than those measured in vacuo; the deviations evidently being caused by a superficial oxydation of the metal in air. Previous investigations have shown that such an oxydation is of much more influence as corresponds to the very small correction for the amount of oxyde formed in the process.

A redetermination of the specific heats of antimony in vacuo and in air did not corroborate the existence of a transformation-temperature at about 413° C., as indicated by BOTTEMA. It seems, however, that the values obtained with an unprotected block of antimony, measured in air, are not identical with those, obtained with granules of antimony, when determined in vacuo. The latter values are 2—1 % smaller than the first ones. Both series of values are, therefore, used in the comparison of the molecular heats of the compounds with the sum of the atomic heats of the composing elements.

The following intermetallic compounds have been investigated: $MgZn_2$, $PdSb$, $PdSb_2$, Pd_3Sb , $PtSb_2$, $PdCu$ and $PdCu_3$. The

differences between the observed molecular heats and the values, calculated from the additive law ($C'_p - \Sigma$), are all negative in the case of the compounds $MgZn_2$, $PdSb$, Pd_3Sb and $PtSb_2$, — these deviations being respectively 1—7 %, 1—4 %, 3—6 %, 7—19 %. They are a function of the temperature; all augmenting with increasing temperatures. The differences are very small in the case of the compound $PdSb_2$ and their algebraic sign is oscillating. It is possible that the compound has been transformed into a solid-solution during the repeated heatings. It may be remarked that beyond any doubt, the preparation having the constitution: $PdCu$, consisted of mixed-crystals, as by means of X-rays it was established that no true compound was present. The deviations from the additive law were very small, with an uncertain (oscillating) algebraic sign; they become somewhat greater above 700° C. As it was an established fact, that in mixtures containing 49,8 at. procents of Pd , the compound still appears, but not so in such containing 49,95 at. procents of Pd , the result of our measurements proves to be in perfect agreement with the fact mentioned, because the preparation used contained more than 50 at. procents of Pd .

The deviations for $PdCu_3$, on the other hand, were positive. Although, the X-rays-spectrogram proved the absence of a true compound (no hyperstructure-lines being found), the procentual values of the deviations are rather high (1—5 %) for mixed crystals. Possible the compound has, to some extent, been formed during the tempering of the mixed-crystals below 600° C. The higher values of ($C'_p - \Sigma$) at 800° C. and 900° C. are not exceptional for mixed crystals.

Nevertheless, the final conclusion from this investigation is, that the molecular heats of true compounds are not in agreement with the additive law, but generally deviate from the values thus calculated by amounts which increase with augmenting temperatures.